

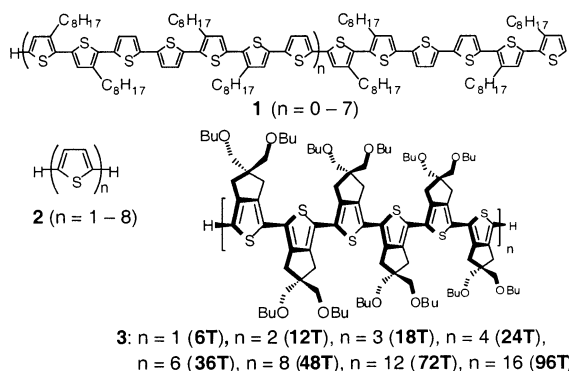
Synthesis and Spectroscopic Properties of a Series of β -Blocked Long Oligothiophenes up to the 96-mer: Reevaluation of Effective Conjugation Length

Tsuyoshi Izumi, Seiji Kobashi, Kazuo Takimiya, Yoshio Aso,* and Tetsuo Otsubo*

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

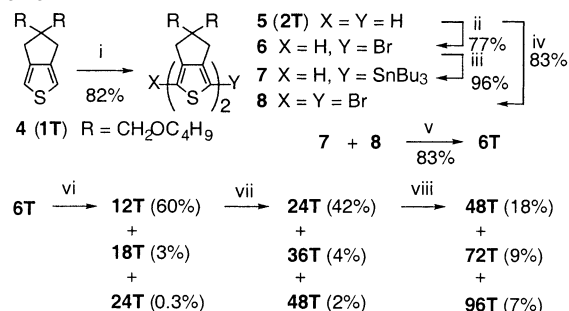
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Structurally well-defined α -conjugated oligothiophenes are of current interest as advanced nanoscale molecules.¹ Our group recently developed the longest series of oligothiophenes **1** up to the 48-mer,² which, in contrast to the limited series of nonsubstituted oligothiophenes **2** up to the octamer,³ provide much information on the conjugation of polythiophenes. To extend them to further higher homologues, these long oligothiophenes need to be functionalized at the terminal α -positions. However, such selective reactions are usually impossible. The β -reactions of oligothiophenes, basically negligible as compared to the α -reactions, become eminent for long oligothiophenes as a result of the statistical increase of the β -sites. The desired α -products are inseparable from the contaminated β -products. To avoid the undesirable β -reactions, we have designed the complete β -blocking of oligothiophenes, which allows the formation of extraordinarily long oligothiophenes **3** (abbreviated to **nT**) up to the 96-mer.



As shown in Scheme 1, the key thiophene monomer **4** (**1T**) substituted by a 2,2-bis(butoxymethyl)-1,3-propanediyl group at both β -sites was prepared in a reasonable yield (41%) through three steps from known 2,5-dibromo-3,4-bis(bromomethyl)thiophene⁴ and converted in 82% yield to the dimer **5** (**2T**) by treatment with butyllithium, followed by oxidative coupling of the lithiated species with iron(II) acetylacetonate. Treatment of **5** with 1 mol equiv of NBS gave the monobromo derivative **6** (77%), which was then converted to the tributyltin derivative **7** (96%). Alternative treatment of **5** with 2 mol equiv of NBS gave the dibromo derivative **8** (83%), which was subjected to a Stille cross-coupling reaction with 2 mol equiv of **7** to give the 6-mer (**6T**) in 83% yield. Subsequent oxidative homocoupling of **6T** with iron(III) perchlorate afforded a mixture of the 12-mer (**12T**, 60%) and the 18-mer (**18T**, 3%) together with a trace amount of the 24-mer (**24T**), which were separated from one another by preparative gel-permeation liquid chromatography (GLPC) using chloroform as an eluent. The **12T** thus isolated was reoxidized with the same reagent under somewhat severe conditions to give the 24-mer (**24T**, 42%), the 36-mer

Scheme 1^a



^a Reagents and conditions: i) ⁿBuLi, THF, -78°C to rt, 0.5 h, then Fe(acac)₃, reflux, 12 h; ii) 1 equiv NBS, DMF-CS₂, rt, 2 h; iii) ⁿBuLi, THF, -78°C to rt, 1 h, then Bu₃SnCl, -78°C to rt, 12 h; iv) 2 equiv NBS, DMF-CS₂, rt, 2 h; v) Pd(PPh₃)₄, xylene, reflux, 8 h; vi) 1 equiv Fe(ClO₄)₃, CHCl₃-CH₃CN, 0°C , 3.5 h; vii) 1.5 equiv Fe(ClO₄)₃, CHCl₃-CH₃CN, rt, 13 h; viii) 2 equiv Fe(ClO₄)₃, CHCl₃-CH₃CN, 50°C , 18 h.

Table 1. Molecular Weights and Electronic Spectra of Oligothiophenes **nT**

compd	MS $M_w/(m/z)^a$	GLPC M_w^b	abs _{max} /nm ^c	flu _{max} /nm ^c
1T	—	382	247.5	nonflu.
2T	590.9 (590.5)	813	313.0	347.6, 360.8
4T	1178.8 (1178.6)	1438	408.5	453.2, 481.6
6T	1768.8 (1768.0)	2028	457.5	514.4, 551.4
12T	3535.8 (3534.7)	4033	506.5	574.6, 622.0
18T	5305.5 (5301.7)	6284	517.0	583.2, 630.0
24T	7068.9 (7068.5)	8620	521.5	585.6, 635.8
36T	10609.1 (10602.0)	14072	524.4, 546.3	587.6, 637.9
48T	14142.5 (14135.5)	20178	525.6, 551.4	588.5, 638.7
72T	21200.1 (21202.6)	30649	526.8, 554.6	590.0, 639.1
96T	28270.2 (28269.3)	47028	527.7, 556.5	590.4, 641.6

^a MS molecular weights were measured by a MALDI-TOF mass spectroscopic instrument using 1,8,9-trihydroxyanthracene matrix. Calculated M_w values are given in parentheses. ^b GLPC molecular weights were determined with the polystyrene standard in THF. ^c Absorption and fluorescence spectra were measured with experimental wavelength errors of 0.2 and 0.4 nm, respectively, in dichloromethane. Only characteristic vibronic peaks are noted.

(**36T**, 4%), and the 48-mer (**48T**, 2%). The repeated oxidation of **24T** successfully gave the 48-mer (**48T**, 18%), the 72-mer (**72T**, 9%), and the 96-mer (**96T**, 7%).

The molecular structures of all the long oligothiophenes **3** were unambiguously characterized by MALDI-TOF MS measurements, and the molecular ion peaks are given in Table 1. The structure determination was also corroborated by the ¹H NMR spectra with appearance of a small but specific singlet resonance signal at δ 6.68 due to the two α -thiophene protons, together with broad large signals corresponding to the numerous protons of the five-membered methylene groups and the pendant butoxymethyl groups. Analytical GLPC using the polystyrene standard confirmed the isolation of

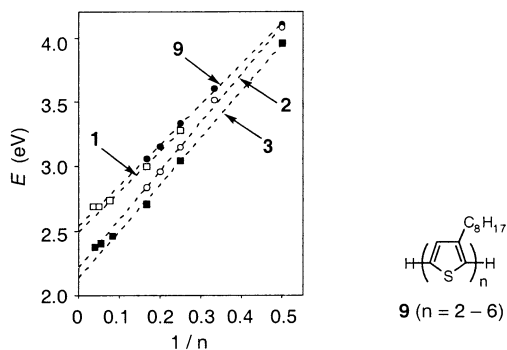


Figure 1. Correlation between electronic transition energies (E) and inverse ring numbers ($1/n$) of oligothiophenes.

these oligomers as single components. Table 1 also shows that the GPC molecular weights of the long oligomers tend to be considerably larger than the actual values. Such inflation of molecular weights as compared to that of the randomly shaped polystyrene standard is characteristic of the type of rodlike long molecules.^{2,5} The GPC molecular weights increase proportionately with the increasing thiophene units in the oligomeric series (Figure S1). This result clearly suggests that the molecular chains of these oligothiophenes are elongated, retaining a rigid rod-type shape. Assuming that it adopts an energetically favorable all-trans conformation with regard to the thiophene-ring linkage, **96T** is estimated to have a chain length of 37.2 nm.

One of the major subjects for studying long oligothiophenes is to establish the concept of an effective conjugation length regulating the characteristics of polythiophenes. Oligothiophenes show a strong π - π^* electron absorption band in the visible region, which is progressively red-shifted with increasing chain length. In the short oligomeric series, there is an excellent linear correlation of the transition energies with the inverse ring numbers, but for the long oligomers, there is a deviation from linearity due to the occurrence of saturation, and the completely saturated point of the red-shift is defined as the effective conjugation length. On the basis of the spectroscopic study of undecithiophenes, Wynberg and co-workers claimed that the effective conjugation is not much longer than 11 repeat units.⁶ However, the later study based on an extrapolation of the transition energy/chain length relationship suggested that the saturation of the effective conjugation be extended to 20 thiophene units.⁷ In the study of the oligothiophenes **1**, we actually observed the continuous red shifts of their absorption spectra up to the 20-mer.² Surprisingly, the absorption spectra of **3** demonstrate that this system continues the red shifts up to the 96-mer (see also Table 1). The emission shifts also show the same tendency. It is worth noting that the electronic absorption band (527.7 and 556.5 nm in solution) of the 96-mer appears at much longer wavelengths than that (438–450 nm in solution and 500–526 nm in solid-state) of the regioregular poly(alkylthiophene)s.⁸ Thus, it is obvious that the effective conjugation length of this system is extended up to 96 thiophene units and much longer than that previously speculated for polythiophenes.

As demonstrated in Figure 1, a good linear relationship between the transition energy and the inverse ring number within the short oligomeric range provides further information on effective conjugation length. Experimental data of the three systems **1**, **2**, and **3** are fitted by eqs 1, 2, and 3.

$$\text{For } \mathbf{1}: E \text{ (eV)} = 2.49 + 3.14/n \quad (1)$$

$$\text{For } \mathbf{2}: E \text{ (eV)} = 2.22 + 3.76/n \quad (2)$$

$$\text{For } \mathbf{3}: E \text{ (eV)} = 2.13 + 3.64/n \quad (3)$$

It is reasonable to consider that the coefficients of the linear equations reflect the effective conjugations of the individual systems.⁹ The coefficient (3.14) for **1** is much smaller than that (3.76) for nonsubstituted oligothiophenes **2**. The low coefficient of **1** means less conjugation of this system, which can be explained in terms of intrachain twisting due to steric demand of the introduced octyl groups. Guillerez and co-workers reported that even regioregular oligo(3-octylthiophene)s **9** show a low coefficient, 3.15, which is in fair accordance with that found for **1**.⁹ In contrast, the coefficient (3.64) of **3** is nearly the same as that (3.76) of **2**, indicating that the coplanarity of the oligomeric backbone of **3** is little disturbed by fusion of the cyclopentane rings.¹⁰ This supports the highly extended conjugation of **3** above-mentioned.

In conclusion, we have succeeded in the development of extraordinarily long oligothiophenes **3** up to the 96-mer. Their spectroscopic measurements evidently indicate that they are highly conjugated like nonsubstituted oligothiophenes and exhibit no convergent limit for the extended conjugation up to the 96-mer yet.

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Supporting Information Available: Experimental procedures and spectroscopic data of **3–8** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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